

TRAPPING PLANETARY NOBLE GASES DURING THE FISCHER-TROPSCH-TYPE SYNTHESIS OF ORGANIC MATERIALS. J. A. Nuth¹ N. M. Johnson¹ A. Meshik² and C. Hohenberg²,

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Introduction: When hydrogen, nitrogen and CO are exposed to amorphous iron silicate surfaces at temperatures between 500 - 900K, a carbonaceous coating forms via Fischer-Tropsch type reactions¹. Under normal circumstances such a catalytic coating would impede or stop further reaction. However, we find that this coating is a better catalyst than the amorphous iron silicates that initiate these reactions^{2,3}. The formation of a self-perpetuating catalytic coating on grain surfaces could explain the rich deposits of macromolecular carbon found in primitive meteorites and would imply that protostellar nebulae should be rich in organic material. Many more experiments are needed to understand this chemical system and its application to protostellar nebulae.

Planetary Noble Gases: If FTT reactions form macromolecular carbonaceous coatings on grain surfaces in the primitive solar nebula, then such reactions could be responsible for trapping ambient nebular gas, including the Planetary Noble Gas component found in many primitive meteorites^{4,6}. As a corollary, if we can show that the planetary noble gases are trapped in such coatings, and measure the trapping efficiency for this process, then we might be able to use measurements of the noble gas content of meteorites and of samples returned from comets and asteroids to estimate the fraction of solar system organics that were produced via such reactions. We have begun to carry out such experiments in our laboratory.

Experiment: The experiments reported here are very simple and were designed to test the relative efficiency of various catalysts as a function of temperature. We have slightly modified our procedure to simultaneously study the trapping efficiency of noble gases as the coatings are produced. A schematic diagram of the closed-cycle apparatus is shown in Figure 1. Following evacuation at room temperature using a liquid-nitrogen-trapped mechanical pump, we fill the system with our gas mixture, begin gas circulation, bring the catalyst up to its working temperature and begin to take our first spectrum. The initial heating rate depends on the intended temperature of the run and the time required to achieve a steady state temperature takes somewhat less than the 30-minutes required to obtain the initial FTIR spectrum (recorded at 2 cm⁻¹ resolution). Using the FTIR spectrometer, we monitor the depletion of CO (2044-2225cm⁻¹), and the formation of methane (2848-3195cm⁻¹), NH₃ (959-970cm⁻¹, 924-936cm⁻¹), CO₂ (2285-2388cm⁻¹) and water

(3959-3530 cm⁻¹). These species are monitored in real time.

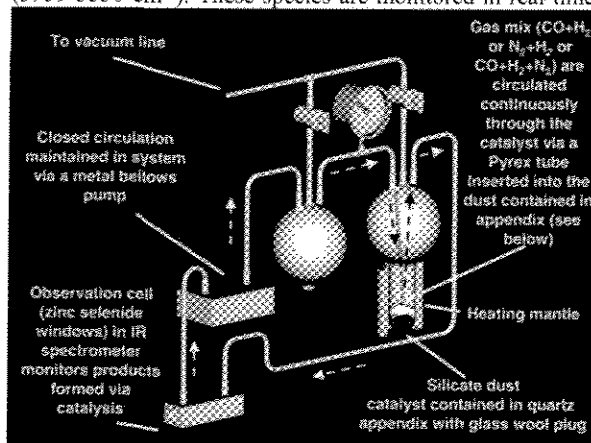


Figure 1. Schematic drawing of the system. The (smoke) catalyst is contained in the bottom finger of a 2-liter Pyrex bulb that can be heated to controlled temperatures. A Pyrex tube brings reactive gas to the bottom of the finger. The gas then passes through the catalyst into the upper reservoir of the bulb, flows through a copper tube at room temperature to a glass-walled observation cell (ZnSe windows) in an FTIR spectrometer and a closed-cycle metal bellows pump returns the sample via a second 2-liter bulb and the Pyrex tube to the bottom of the catalyst finger to start the cycle over again. The gas mixture initially consists of 75 torr N₂, 75 torr CO & 550 torr of H₂. Total pressure is reduced as the reaction proceeds, is monitored via a diaphragm gauge placed in-line between the two bulbs and has been observed to vary from highs near 750 torr to low pressures near 600 torr. To this gas mixture we now add 25 torr of a rare gas mixture consisting of 49% Ne, 49% Ar, 1% Kr and 1% Xe.

Time, Temperature and Pressure: We are aware that the pressures to be used in our experiments are much higher than those in the solar nebula and are also aware that this difference could affect the results of our experiments. We would love to duplicate nebular conditions and run our experiments continuously for several hundred years but such timescales are impractical for many reasons. On average our experiments run for times from several days to several weeks. If an average experiment lasts for a week (6.05 x 10⁵s) but should last for a century (3 x 10⁹s) to duplicate conditions found in protostellar nebulae, we can get the same

number of reactive collisions with our surfaces by increasing the pressure by a factor of $\sim 5 \times 10^3$, from about 10^{-4} - 10^{-3} atm in the nebula to from 0.5 to 5 atm in our experiments. The experiments that we run at 1 atm underestimate the number of collisions experienced by an average grain surface in the nebula in 100 years. Grains could circulate in such nebulae for 10^4 years or longer (but at differing temperatures). We consider pressure to be a proxy for time and ignore its effects on products of these initial experiments, though we do intend to vary pressure in future experiments.

We have another temporal consideration as well. When experiments are run at 873K, we can make two runs per week. Since we require 15 – 20 experimental runs to make a significant coating (10% by mass C) we therefore require approximately 2 months to complete experiments at 873K. At 773K we can make two runs in just over three weeks, so an experiment requires ~ 5 months to complete. At 673K these experimental runs take over 3 weeks each and we therefore require nearly 11 months to complete a study. At 473K a run requires more than 8 weeks; nearly 3 years to finish a single experiment. Yet in the ideal case, we would like to perform experiments at much lower temperatures than these, where trapping is likely to be more efficient but the formation of the macromolecular coating is much slower. Unfortunately, until we can afford to run a single experiment for several years, we must be content to extrapolate the results of higher temperature experiments to those more prevalent in the solar nebula.

Results: Our first experiments used amorphous iron silicate smokes as the catalyst and were carried out at 873K. The samples were sent to Washington University for analyses. We determined the bulk concentration of Xe, Kr and Ar in a single extraction step at $\sim 1800^\circ\text{C}$. These concentrations are $2.18\text{E-}07$ ccSTP/g for ^{132}Xe , $3.35\text{E-}07$ ccSTP/g for ^{84}Kr , and less than $3.7\text{E-}08$ ccSTP for ^{36}Ar . The isotopic fractionation is \sim linear: 0.7%/amu for Xe and 1.5%/amu for Kr compared to terrestrial atmospheric values. The sign of this fractionation is unusual: in both gases the light isotopes are more abundant.

We are currently completing an experiment that also used amorphous iron silicate smoke as a catalyst, but that was run at 673K over the past year. This sample will also be sent to Washington University for analysis and the results compared with the higher temperature experiments. Results of these experiments will be presented at the conference together with information on the structure of the carbonaceous coating on the grain surfaces.

References: [1] Hill. H. G. M. and Nuth, J. A. (2003) *Astrobiology* **3**, 291 – 304. [2] Nuth J.A., Johnson, N.M. and Manning, S., 2008a *Ap. J. (Lett.)* **673** L225 - L228. [3] Nuth J.A., Johnson, N.M. and Manning, S., 2008b in *Organic Matter in Space*, Proceedings IAU Symposium No. 251, 2008 (S. Kwok & S. Sandford, eds.) pp. 403 – 408. [4] Huss G. R., Lewis R. S., and Hemkin S. (1996) *Geochim. Cosmochim. Acta* **60**, 3311-3340. [5] Wieler R., Anders E., Baur H., Lewis R.S., & Signer P. (1991) *Geochim. Cosmochim. Acta* **55**, 1709-1722. [6] Wieler R., Anders E., Baur H., Lewis R.S., & Signer P. (1992) *Geochim. Cosmochim. Acta* **56**, 2907-2921.